Kojindani, Sendai, Japan
Identical pieces in immediate contact but totally different corrosion products
Everything corrodes (oxidizes, sulfidizes, rusts, tarnishes) - corrosion is inevitable, even for organic and inorganic materials such as glass or slag inclusions.
Corrosion-2

- Even precious metals-Au, Pt, Pd (restricted)
- Economic impact is huge-$296 billion (Battelle/NIST Report, April 1995)
- Coating protection (Galvanizing, Galvalume, Anodizing) significantly slows corrosion with resulting enormous reduction in cost
Emphasis on coatings research in the 1950’s shifted research focus away from basic corrosion/microstructure studies (important for archaeological/conservation work)

- dry vs. aqueous
  - low temperature (room) vs. high

- Kinetics - linear, logarithmic, parabolic
Fe-Fe$_3$C Phase diagram

Composition (at% C)

Temperature (°C)

(Fe)

Composition (wt% C)

1538°C
1493°C
1394°C
912°C
727°C

γ, Austenite
γ, Fe$_3$C
α, Ferrite
Cementite (Fe$_3$C)

α + Fe$_3$C
γ + L
δ

L

2.14
4.30

0.76
0.022
Phase diagrams vs. Predominance diagrams

**FIGURE 11.13**
Comparison of (a) a phase diagram with (b) the analogous predominance diagram plotted in $\left(\log P_{O_2} - 1/T\right)$ space for the Fe-O system.

R.T.DeHoff, Thermodynamics in Materials Science (1993)
Predominance diagrams take the form of a cell structure with areas that represent domains of predominance of a particular component separated by lines that are the limits of predominance of competing components.

While a predominance diagram (such as a Pourbaix diagram) may provide an approximate representation of a phase diagram they are not identical to phase diagrams. Domains of predominance displayed in these diagrams are not identical with the domains of stability normally presented in phase diagrams.

Boundary lines on a predominance diagram represent 50% lines for the bounding reactions. Phase boundaries on phase diagrams represent bounding conditions for the equilibrium presence of (n) phases (1, 2, 3, etc.) with any point inside a multiple phase region indicative of the quantitative amount of the phases.
Predominance diagrams have only one component labeled in each field.

Phase diagrams have different phases identified in each field such that if a field is labeled as (n) phases, then the adjacent fields have (n+1) or (n-1) phases.

The location within a component field in a predominance diagram does not indicate the quantitative relative amount of that component other than that it is the major species.

The location within a multiphase (n>1) region in a phase diagram gives a quantitative indication of the relative amount of each phase within that phase field. For example, in a binary phase diagram the position along horizontal tie lines in two-phase fields indicates the relative percentage of each of the phases indicated by the ends of the tie line.
“Electron Number Diagrams”

Fig. 3. Electron number diagram for the copper system. Intersection of the three-dimensional figure with the pH = 8.81 plane. Note the eutectic reaction between Cu₂O, the aqueous phase, and CuO along the line IJK.
Cu single crystal sphere oxidizes at different rates in Different crystallographic directions.
High Temperature Oxidation Kinetics (Simple Models)

The parabolic rate law assumes that the diffusion of metal cations or oxygen anions is the rate controlling step.

\[ x^2 = k_p t + x_0 \]

The rate constant, \( k_p \), changes with temperature according to an Arrhenius type relationship. Experimentally, there is also a cubic law similar to this case (ex., Cu)

The logarithmic rate law is an empirical relationship with no fundamental underlying mechanism.

\[ x = k_e \log(ct + b) \]

The linear rate law is also an empirical relationship that is applicable to the formation and build-up of a non-protective oxide layer.

\[ x = k_L t \]
Red-Ox reactions

‘Galvanic cells’ produce electricity due to spontaneous reaction

‘Electrolytic cells’ require electricity to drive a non-spontaneous chemical reaction

Oxidation at ‘anode’
Reduction at ‘cathode’

Cathode is now negative
**Standard reduction potentials**

Measurements made with respect to the standard hydrogen electrode give standard values for all other half reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{E}^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_2(g) + 2 \text{e}^- = 2 \text{F}^- )</td>
<td>+2.87</td>
</tr>
<tr>
<td>( \text{Cl}_2(g) + 2 \text{e}^- = 2 \text{Cl}^- )</td>
<td>+1.36</td>
</tr>
<tr>
<td>( \text{Ag}^+ + \text{e}^- = \text{Ag} (s) )</td>
<td>+0.80</td>
</tr>
<tr>
<td>( \text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+} )</td>
<td>+0.77</td>
</tr>
<tr>
<td>( \text{O}_2(g) + 2 \text{H}_2\text{O} + 4 \text{e}^- = 4 \text{OH}^- )</td>
<td>+0.40</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2 \text{e}^- = \text{Cu} (s) )</td>
<td>+0.34</td>
</tr>
<tr>
<td>( 2 \text{H}^+ + 2 \text{e}^- = \text{H}_2(g) )</td>
<td>0.000</td>
</tr>
<tr>
<td>( \text{S}(s) + 2 \text{e}^- = \text{S}^2^- )</td>
<td>-0.48</td>
</tr>
<tr>
<td>( \text{Zn}^{2+} + 2 \text{e}^- = \text{Zn} (s) )</td>
<td>-0.76</td>
</tr>
<tr>
<td>( 2 \text{H}_2\text{O} + 2 \text{e}^- = \text{H}_2(g) + 2 \text{OH}^- )</td>
<td>-0.83</td>
</tr>
<tr>
<td>( \text{Na}^+ + \text{e}^- = \text{Na} (s) )</td>
<td>-2.71</td>
</tr>
<tr>
<td>( \text{Cs}^+ + \text{e}^- = \text{Cs} (s) )</td>
<td>-2.92</td>
</tr>
</tbody>
</table>

Species on left easiest to reduce; species on right hardest to oxidize.

Species on left hardest to reduce; species on right easiest to oxidize.

Leads to the ‘electrochemical series’ — ‘noble’ metals closest to the top. 
The Pourbaix (E-pH) Diagram

Potential

2H₂O = O₂ + 4H⁺ + 4e⁻
Equilibrium potential falls as pH increases

2H⁺ + 2e⁻ = H₂
Equilibrium potential falls as pH increases

pH = - log [H⁺]
The Pourbaix (E-pH) Diagram

Potential

O₂ is stable

H₂O is stable

H₂ is stable

pH
Pourbaix diagrams include information on solvent stability, and information about oxidizing vs. reducing and acidic vs. alkaline conditions.
“corrosion” defined as amount of permissible metal dissolution
\[ \log(a_{\text{species}}) = -6 = \text{“no corrosion for all practical purposes”} \]
Pourbaix Diagrams - Alloys

Pourbaix diagrams for systems with only a single metallic species such as Ag, Cu, Fe, Sn or Zn can be easily determined and tabulated.

Pourbaix diagrams for systems with more than one metal species are difficult (or nearly impossible) to obtain and requires computer calculation.

For example, even the Cu-Ni system which has complete solid solubility is difficult because of the varying thermodynamic activity across the Cu-Ni system.

The Cu-Sn (bronze) system is difficult because of the intermediate phases that occur.
Pourbaix diagram for Cu-Sn-H$_2$O (F*A*C*T) w/o $\varepsilon$-Cu$_3$Sn phase
Pourbaix diagram for Cu-Sn-H₂O (F*A*C*T) with ε-Cu₃Sn phase
Pourbaix Diagram for Iron

- Fe metal stable
- Fe oxides stable
- Fe$^{2+}$ stable
Electrolytic Reduction
Conservation of an Iron Cannon from Finland

Lifting the cannon

Mechanical cleaning and removal of graphitized layer

Electrolytic reduction
Endeavor iron cannon after electrolytic reduction
Chinese mirror with almost no corrosion
Chinese vessel showing both Azurite and Malachite
Corrosion along grain boundaries & mechanical twins
Cu-8 w/o Sn bronze (Scott)
Diffusion is more rapid along grain boundaries & surfaces

Fig. 2.27  Diffusion in a polycrystalline metal.

Fig. 6-1. Values of the self-diffusion coefficient obtained for silver using single-crystal and polycrystal samples. (After D. Turnbull, in "Atom Movement," p. 129, ASM, Cleveland, 1951.)
Corrosion along dendrites in a Chinese bronze arrowhead
Interdendritic corrosion

Cuprite

Malachite

Copper

QuickTime™ and a TIFF (LZW) decompressor are needed to see this picture.
Roman Coin with Bronze Disease
Bronze disease

Figure 6. Schematic presentation of normal patination layers on ancient bronze and the nature of "bronze disease".
Corrosion in Plain Iron-Carbon Alloys

- Low to Medium Carbon Iron (0-0.7 wt% C)
- Pearlitic Iron (0.7 wt% C)
- High Carbon Iron (0.7-2 wt% C)
- Cast Iron (>2 wt% C)
Classification of Ghost Structures (B. Scott, 1988)

- **Remanent Structures**: complete grains or aggregates of metal surviving intact
- **Partial Replacement Structures**: grain fragments with majority of structure converted to corrosion products
- **Fossil Structures**: form alone is preserved but with no surviving metal
Fig. 5.55  A pearlite colony advancing into an austenite grain. (After L.S. Darken and R.M. Fisher in Decomposition of Austenite by Diffusional Processes, V.F. Zackay and H.I. Aaronson (Eds.), by permission of The Metallurgical Society of AIME.)
Tel Miqne Knife
an example of changing corrosion conditions
Baqah Iron Artifacts

Corroded Fe object with Residual spheroidized Fe$_3$C

Spheroidized pearlite and very large carbides

Light microscope

SEM
Sword from Vered Jericho
SEM (SE) Residual Pearlite
EPMA EDS Survey map
EPMA WDS maps

Fe  Si  O  C
Early Cast Iron - China
Progressing corrosion outlines microstructure without etching
Corrosion and Authentication

1. Single phase alloy (ex., Cu, bronze, low C iron)
   - High angle grain boundaries, mechanical twin/slip interfaces (usually, not annealing twins)
   - Dendrites, especially those due to segregation during solidification
   - Versus uniform corrosion front typical of more rapid high temperature processes or in very aggressive solutions where rate of defect interface attack similar to rate of bulk attack

2. Multiphase alloy (ex., High Sn-bronze, Fe-C steel)
   - Ghost structures
Abstract

This talk will present an introductory view of the very complicated and diverse field of corrosion of metallic materials. The presentation will first cover the fundamentals of oxidation of a single metallic species and highlight the kinetics and morphology of growth. We will demonstrate the relationship between Pourbaix Diagrams, predominance diagrams, phase diagrams and a new concept termed “electron number diagrams”. We will finally focus on the complicated corrosion processes that take place in typical archaeological iron objects.